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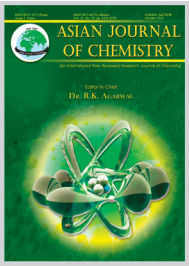

Microwave Synthesis of Ag-$PbWO_4$/Zeolite Composites Assisted by A Solid-State Metathetic Approach†

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Ag-$PbWO_4$/zeolite composites were synthesized using a solid-state metathetic method with microwave irradiation. The characteristics of the solid-state metathetic reaction and the formation of the high lattice energy by-product of NaCl were found to drive the reaction for Wolframite-type $PbWO_4$ toward completion. The Ag-$PbWO_4$/zeolite composites were formed completely at 600 ºC. Monoclinic-like crystals of $PbWO_4$ were primarily co-mixed with porous zeolite-A. Small spherical silver particles were immobilized in the porous $PbWO_4$/zeolite-A matrix.

Key Words: Solid-state metathetic, Ag-$PbWO_4$/zeolite composites, Microwave irradiation.

INTRODUCTION

Metal tungstates has attracted extensive attention because of their particular importance in investigating the sizes and shape-dependent properties as well as their immobilization in porous materials for potential applications[1,2]. For tungstate materials to be used for practical applications, versatile characteristics are required for the particle size distribution and morphology of the particles. Metal tungstates have attracted considerable attention for potential applications as a scintillator, microwave devices, luminescent material and photocatalyst[3-7]. The physical, chemical and photochemical properties of metal tungstates are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of metal tungstates are prepared by a range of processes, such as a solid-state reaction[8,9], co-precipitation[10-12], a molten salt method[13,14], a hydrothermal reaction[15,16], a combustion method[17], a mechano-chemical method[18], a polymeric precursor[19], microwave irradiation[20-22].

Solid-state metathetic (SSM) reactions involve the exchange of atomic/ionic species, where the driving force is the exothermic reaction accompanying the formation of NaCl with high lattice energy. Solid-state metathetic reactions occur so rapidly that the exothermic reaction is essentially used to heat the solid products. Solid-state synthesis of materials by the metathetic route is a simple method of synthesis, cost-effective, high yield and easy scale up and is emerging as a viable alternative approach for synthesizing high-quality novel inorganic materials in a short time[23,24]. The solid-state metathetic approach assisted by microwave irradiation has been applied successfully to the synthesis of metal tungstates of Wolframite-type[25-29]. The well-defined particle features of the Ag-$PbWO_4$/zeolite-A porous composites are required for the immobilization features for potential applications the potential applications. Silver-incorporated $CdWO_4$/zeolite-A porous composites are expected to have excellent adsorption and synergy effects in an immobilization mechanism of metallic catalysts for a wide range of applications, such as sensors, photocatalysts, luminescence, antibacterial matrices and optical effects in the UV and visible region.

In this study, Ag-$PbWO_4$/zeolite composites were synthesized using a solid-state metathetic (SSM) method with microwave irradiation. The characteristics of the solid-state metathetic reaction and the formation of a high lattice energy by-product NaCl were discussed. The Ag-$PbWO_4$/zeolite composites were immobilized from mixed metathetic precursors at moderate temperatures. The crystallization process, thermal decomposition and morphology of the synthesized Ag-$PbWO_4$/zeolite composite powders were evaluated.

EXPERIMENTAL

Fig. 1 shows a flow chart for the synthesis of Ag-$PbWO_4$/zeolite composites from the solid-state metathetic method using

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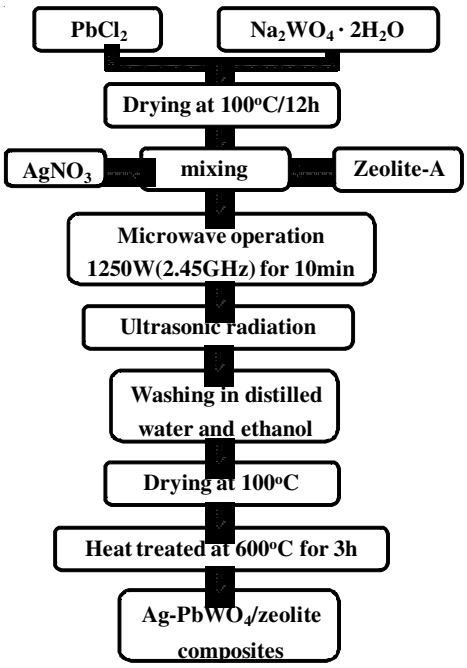


Fig. 1. Flow chart for the synthesis of Ag-$PbWO_4$/zeolite-A porous composites from the solid-state metathetic method using microwave irradiation

microwave irradiation. $PbCl_2$ and $Na_2WO_4{\cdot}2H_2O$ of analytic reagent grade were used to prepare the metal tungstate compound. The preparation of metal tungstates were carried out by reacting well-ground mixtures of $PbCl_2$ and $Na_2WO_4{\cdot}2H_2O$ for $PbWO_4$ at a molar ratio of 1:1. The sample mixtures were dried at 100 ºC for 12 h and 5 wt % $AgNO_3$ and 25 wt % synthetic zeolite-A were then added. The samples were placed into crucibles and exposed to domestic microwave (Samsung Electronics Corp. Korea) operating at a frequency of 2.45 GHz and a maximum out-put power of 1250 W for 10 min. The samples were treated with ultrasonic radiation and washed many times with distilled water and ethanol to remove the sodium chloride reaction by-product. The samples were dried at 100 ºC in an oven. Heat-treatment of the samples was performed at 600 ºC for 3 h.

The phase existings in the particles after the solid-state metathetic reactions and heat-treatment were identified by XRD (D/MAX 2200, Rigaku, Japan). FTIR (Nicolet IR200, Thermo Electron corporation, USA) was used to examine the thermal-decomposition behavior of the solid-state metathetic reaction and the obtained particles over the frequency range, 4000-400 cm^{-1}. The microstructure and surface morphology of the Ag-$PbWO_4$/zeolite-A porous composite powders were observed by scanning electron microscopy (JSM-5600, JEOL, Japan) and energy-dispersive X-ray spectroscopy (EDS).

RESULTS AND DISCUSSION

Fig. 2 shows FT-IR spectra of the Ag-$PbWO_4$/zeolite composites after (a) microwave metathetic reaction (Ag-$PbWO_4$-Z-m) and (b) heat-treatment at 600 ºC for 3 h (Ag-$PbWO_4$-Z-m600). The absorption bands at 532 and 473 cm^{-1} can be assigned to symmetric and asymmetric deformation mode of Pb-O in PbO_6 octahedra. The absorption bands with their maxima at 710 and 633 cm^{-1} are due to the stretching modes

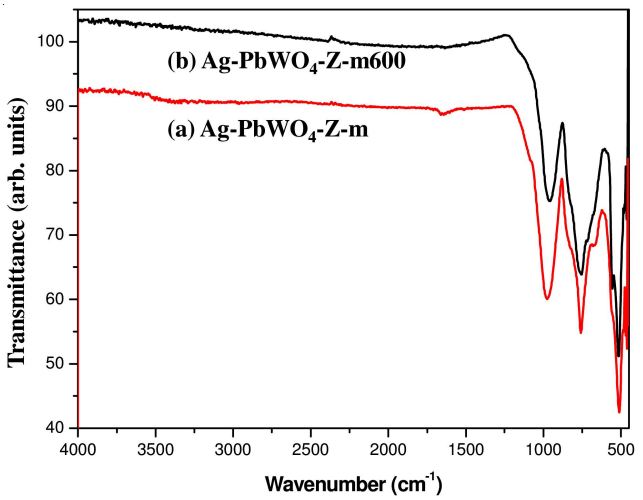


Fig. 2. FT-IR spectra of the Ag-$PbWO_4$/zeolite-A porous composites after (a) solid-state metathetic reaction and (b) heat-treatment at 600 ºC for 3 h

of W-O in WO_6 octahedra. The bands at 877 and 834 cm^{-1} were due to symmetrical vibrations of bridge oxygen atoms of the Pb-O-W groups.

Fig. 3 shows SEM images of the Ag-$PbWO_4$/zeolite composites after (a) microwave metathetic reaction and (b) heat-treatment at 600 ºC for 3 h. Fig. 3(a) shows SEM images of the Ag-$PbWO_4$/zeolite composites synthesized by solid-state metathetic reaction after removing the NaCl. $PbWO_4$ crystallizes in Wolframite crystal structures. Presence of sodium chloride confirms the reaction has proceeded in solid-state metathesis way. Parhi *et al.*[25] reported the microwave metathetic synthesis of various metal tungstates and showed that microwave radiation provided the energy required to fabricate fine particles with a controlled morphology and the formation of the product in a green manner without the generation of solvent waste. In Fig. 3(b), the SEM images of Ag-$PbWO_4$/zeolite composites after heat-treatment at 600 ºC for 3 h show the well crystallized $PbWO_4$ on the zeolite-A synthesized by a solid-state metathetic reaction. The monoclinic-like crystals of $PbWO_4$ were primarily co-mixed with Ag on the porous zeolite-A surfaces. The spherical small particles of silver were well immobilized in the porous $PbWO_4$/zeolite-A composites matrix. Solid state metathesis reactions, such as $PbCl_2 + Na_2WO_4 \rightarrow PbWO_4 + 2NaCl$, involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction and formation of NaCl with a high lattice energy. The thermodynamic basis for such metathetic reactions has been reported[25,30-32]. The enthalpy and free energy change associated with the formation of tungstates favour the metathesis reaction and the enthalpy change is indeed the driving force for the metathesis involving the formation of NaCl. Solid-state metathetic reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products, usually raising the alkali halide near or above its normal boiling point and have been recognized to be approximately adiabatic in nature[33].

Fig. 4 shows (a) EDS patterns, (b) quantitative compositions, (c) a SEM image and (d) quantitative results of the synthesized Ag-$PbWO_4$/zeolite composites at 600 ºC for 3 h.

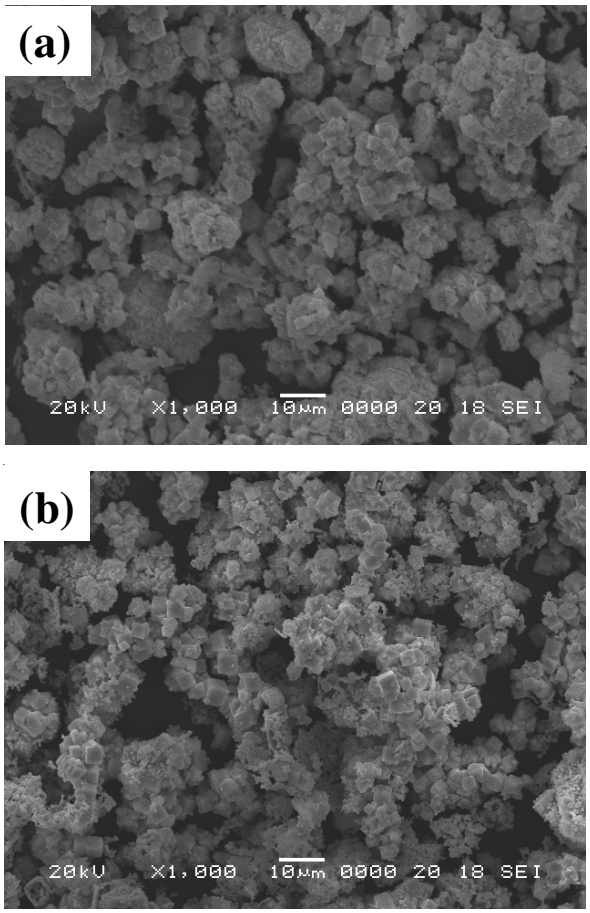
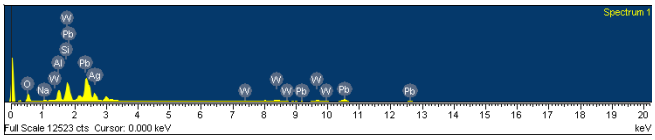


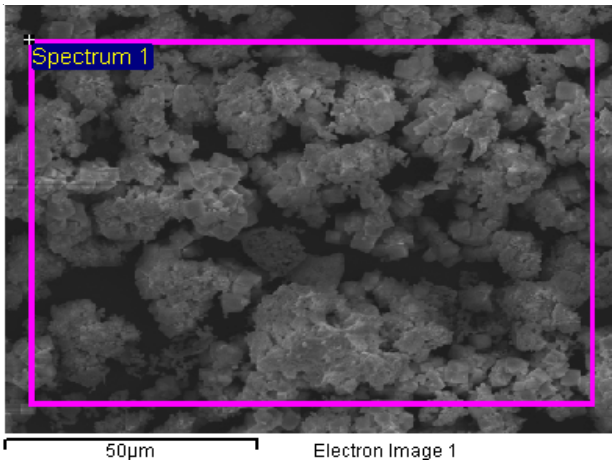
Fig. 3. SEM images of the Ag-$PbWO_4$/zeolite-A porous composites after (a) solid-state metathetic reaction and (b) heat-treatment at 600 ºC for 3 h



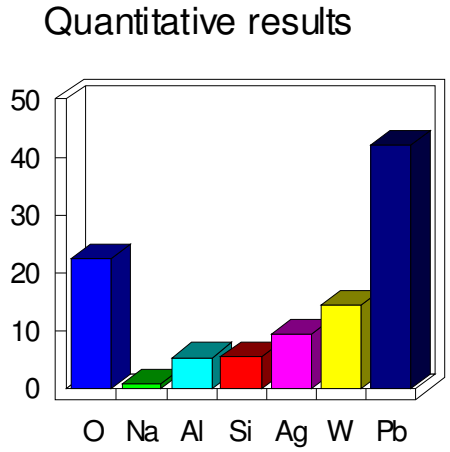
(a)

Spectrum	In stats.	O	Na	Al	Si	Ag	W	Pb	Total
Spectrum 1	Yes	22.50	0.85	5.41	5.51	9.43	14.23	42.07	100.00
Mean		22.50	0.85	5.41	5.51	9.43	14.23	42.07	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.		22.50	0.85	5.41	5.51	9.43	14.23	42.07	
Min.		22.50	0.85	5.41	5.51	9.43	14.23	42.07	

(b)



(c)



(d)

Fig. 4. EDS patterns (a), quantitative compositions (b), a SEM image (c) and quantitative results (d) of the synthesized Ag-$PbWO_4$/zeolite-A porous composites

The EDS patterns and quantitative compositions of the synthesized Ag-$PbWO_4$/zeolite composites were composed of Ag, $PbWO_4$ and zeolite-A. For tungstate materials to be used for practical applications, versatile characteristics are required for the particle size distribution and morphology of the particles. The well-defined particle features of the Ag-$PbWO_4$/zeolite composites synthesized by solid-state metathetic reactions have control over the morphology of the final particles and can be used for such technological applications. Owing to the enthalpy change by the driving force for the metathetic formation of NaCl, the solid-state metathetic reactions affect not only the morphology of the $PbWO_4$ particles, but also the formation of functional zeolite and Ag immobilized in the porous composite matrix. Therefore, a variation of metathetic reactions of

$$PbCl_2 + Na_2WO_4 \longrightarrow PbWO_4 + 2NaCl$$

is required to control the well-defined particle features of the Ag-$PbWO_4$/zeolite composites.

Conclusion

Ag-$PbWO_4$/zeolite composites were synthesized using a solid-state metathetic (SSM) method with microwave irradiation. The Ag-$PbWO_4$/zeolite composites at 600 ºC for 3 h were completed entirely at 600 ºC. The well crystallized $PbWO_4$ on the zeolite-A synthesized by a solid-state metathetic reaction. The monoclinic-like crystals of $PbWO_4$ were primarily co-mixed with Ag on the porous zeolite-A surfaces. The spherical small particles of silver were well immobilized in the porous $PbWO_4$/zeolite-A composites matrix. The enthalpy change favours the metathesis reaction and the enthalpy change is indeed the driving force for the metathesis involving the formation of NaCl. Solid-state metathetic reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products of Ag-$PbWO_4$/zeolite composites.

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